

FACT SHEET

New Developments in 1,4-Dioxane Site Management

SERDP Project ER-2307

NOVEMBER 2016

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1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)			
01/11/2016	Fact Sheet				
4. TITLE AND SUBTITLE		5a. CONTRACT NUMBER W912HQ-13-0062			
New Developments in 1,4-Dioxane Site Management		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
		5d. PROJECT NUMBER ER-2307			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) GSI Environmental, Inc. 2211 Norfolk, Suite 1000 Houston, TX USA 77005		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Strategic Environmental Research and Development Program 4800 Mark Center Drive Suite 17D03 Alexandria, VA 22350-3605		10. SPONSOR/MONITOR'S ACRONYM(S) SERDP			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES N/A					
14. ABSTRACT New research is changing the conventional conceptual model for how the emerging contaminant 1,4-dioxane behaves following its release to the environment. This fact sheet summarizes the results of a recent project sponsored by the Strategic Environmental Research and Development Program (SERDP) that was designed to develop a more informed conceptual model for 1,4-dioxane, especially in comparison to co-occurring contaminants like chlorinated solvents. A combination of data mining, modeling, and both bench-scale and field scale studies was used to meet the project objectives.					
15. SUBJECT TERMS 1,4-dioxane, chlorinated solvents, data mining, modeling, bench-scale studies, field scale studies, attenuation, chemical oxidation, enhanced bioremediation, site management.					
16. SECURITY CLASSIFICATION OF: a. REPORT b. ABSTRACT c. THIS PAGE		17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON David Adamson	
Unclassified	Unclassified	UU	UL	8	19b. TELEPHONE NUMBER (Include area code) (713) 522-6300

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FACT SHEET

New Developments in 1,4-Dioxane Site Management

INTRODUCTION: New research is changing the conventional conceptual model for how the emerging contaminant 1,4-dioxane behaves following its release to the environment. This fact sheet summarizes the results of a recent project sponsored by the Strategic Environmental Research and Development Program (SERDP) that was designed to develop a more informed conceptual model for 1,4-dioxane, especially in comparison to co-occurring contaminants like chlorinated solvents. A combination of data mining, modeling, and both bench-scale and field-scale studies was used to meet the project objectives. The goal was to use the results of this study as a basis for improved decision making and management of 1,4-dioxane contaminated sites.

SUMMARY: The study established that 1,4-dioxane plumes are generally dilute and frequently similarly-sized or shorter than co-occurring chlorinated solvent plumes. Combined with evidence for attenuation, the results indicate that there is less risk of uncontrolled 1,4-dioxane plumes than originally anticipated. The results also suggest that many 1,4-dioxane sites may no longer have true source zones and that much of the remaining mass may be present in low-permeability regions of the aquifer. As a result, conventional treatment may not be cost-effective or technically practical, and alternative management strategies such as natural attenuation may be more effective than previously thought.

FINDING #1: 1,4-Dioxane plumes are not as large as expected. 1,4-dioxane is highly soluble and does not strongly sorb. These properties have led to a concern that 1,4-dioxane plumes will be long, particularly when compared to chlorinated solvents that may co-occur at these sites. Using geospatial analysis of groundwater monitoring data from the California GeoTracker database, a median 1,4-dioxane plume length of 269 m was established ($n = 108$ sites). At sites where both 1,4-dioxane and chlorinated solvents were detected ($n= 105$), the 1,4-dioxane plume was estimated to be longer than the chlorinated solvent plume(s) at only 21% of the sites (**Figure 1**). At 56% of the sites, the chlorinated solvent plume (typically 1,1-DCE and/or TCE) was longer.

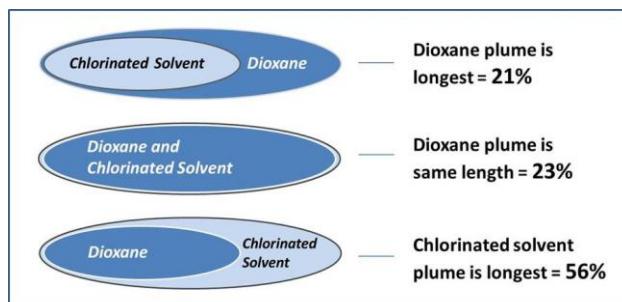
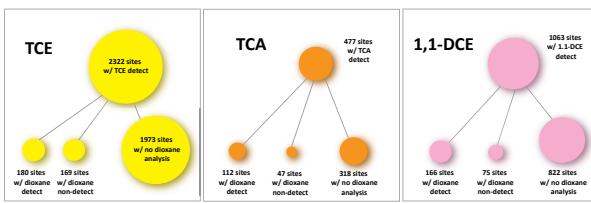


Figure 1. Frequency of 1,4-dioxane plume lengths exceeding chlorinated solvent plume lengths at sites with co-occurring compounds ($n=105$ sites; all in California) (updated from Adamson et al., 2014).

IMPLICATIONS FOR SITE MANAGEMENT: The data suggest that 1,4-dioxane plumes are less likely to extend beyond current monitoring networks (which were designed for chlorinated solvents) than originally feared. This finding is likely related to natural attenuation and containment of decades-old releases of chlorinated solvents and 1,4-dioxane that have been migrating along similar flowpaths and environments. Also, TCE usage at

many sites likely predates the release of 1,4-dioxane, giving TCE (and its by-products) a potential "head-start". However, careful long-term monitoring of 1,4-dioxane plume stability is important, even at sites with relatively short plumes. Given 1,4-dioxane's high migration potential, there is a possibility that 1,4-dioxane plumes at some sites will eventually "catch up" to the chlorinated solvent plumes.

FINDING #2: Based on the observed co-occurrence of 1,4-dioxane and chlorinated solvents, there are probably many "unidentified" 1,4-dioxane plumes. 1,4-dioxane is expected to co-occur with chlorinated solvents based on its use as a stabilizer (for 1,1,1-TCA) and the historic switching between various solvents (e.g., TCE to 1,1,1-TCA, then back to TCE) that occurred at many sites. During the site survey, 1,4-dioxane was detected at 193 sites (of 589) where it was analyzed, with TCE being the most frequently detected co-occurring contaminant (93%), followed by 1,1-DCE (86%) and TCA (58%). At sites where 1,4-dioxane was included in the analytical program, it was detected at 52% of sites containing TCE, 70% of sites containing 1,1,1-TCA, and 69% of sites containing 1,1-DCE (69%) (**Figure 2**). The project results confirmed earlier studies on contaminant co-occurrence (Anderson et al., 2012). However, a key difference was that this study identified a large number of sites with chlorinated solvents where 1,4-dioxane has not been analyzed, ranging from 67% to 85% for this set of constituents. For example, no 1,4-dioxane analyses were conducted at 318 (67%) of the sites where 1,1,1-TCA was detected. Similarly, there were 572 sites with 1,1-DCA but non-detectable levels of TCA where no dioxane analyses had been completed. Based on the co-occurrence data, this means that (at the time of this study) there were several hundred sites in California alone where 1,4-dioxane plumes had yet to be identified and characterized.



Evidence for large number of “unidentified” dioxane sites:
 $(318 \text{ sites}) * (75 \text{ of TCA sites w/ dioxane}) = 239 \text{ “unidentified” dioxane sites}$

Figure 2. 1,4-dioxane co-occurrence data from California sites, with example of potential “unidentified” dioxane plumes at sites where 1,1,1-TCA is present but 1,4-dioxane has not been analyzed (updated from Adamson et al., 2014).

IMPLICATIONS FOR SITE MANAGEMENT. There is a high likelihood that 1,4-dioxane is present at many sites where chlorinated solvents have been detected in groundwater. The data suggest that the majority of sites have yet to include 1,4-dioxane in monitoring programs. While there may be a technical justification for not measuring 1,4-dioxane at a site with mostly TCE, there may be limited historical records of site-specific chlorinated solvent usage. Therefore, prudence would suggest that 1,4-dioxane be included in monitoring programs at all chlorinated solvent sites, particularly those where 1,1,1-TCA degradation products (e.g., 1,1-DCA, 1,1-DCE) are present. Given the potential for sub-ppb regulatory action levels, implementing a thorough characterization and monitoring program is key to eliminating any potential risk to receptors.

FINDING #3: Most 1,4-dioxane sites are dilute. 1,4-dioxane was detected at 193 individual sites included in the survey. The median maximum historical 1,4-dioxane concentrations at these sites was 365 µg/L (10th percentile = 9 µg/L; 90th percentile = 13,460 µg/L). This value is approximately three orders of magnitude higher than the drinking water screening level of 0.67 µg/L for 1,4-dioxane. These results supported the conventional conceptual model that the large majority of plumes are relatively dilute, but only 11% were longer than 1 km. Similar results were found for TCE.

IMPLICATIONS FOR SITE MANAGEMENT: The results support the conventional conceptual model that 1,4-dioxane plumes are dilute (though not necessarily long). As a result, it is more difficult to identify a “high-value” target for aggressive source treatment, and in fact it may be difficult to identify the source itself at some sites. The cost-effectiveness of 1,4-dioxane source treatment (e.g., mass removed per dollar spent) is likely to be poor in most cases, and alternative approaches are likely to be preferable where possible.

FINDING #4: Storage of 1,4-dioxane in lower permeability soils likely contributes to its long-term persistence Modeling was used to establish that, like chlorinated solvents, diffusion of 1,4-

dioxane mass in and out of lower-permeability (low-k) soils (e.g., silts, clays) can be an important fate and process for this compound. During a typical release scenario, 1,4-dioxane was actively loading the low-k layer within the source zone for only a short period (<3 years) relative to 1,1,1-TCA due to 1,4-dioxane’s high effective solubility. Despite this short loading period, the mass of 1,4-dioxane stored within the low-k source zone, as well as the groundwater concentration resulting from back diffusion, was consistently larger than that predicted for 1,1,1-TCA.

Even 80 years after release, the 1,4-dioxane concentration resulting from back diffusion (> 100 µg/L) was still orders-of-magnitude higher than potentially-applicable criteria (Figure 3). Diffusion also contributed to higher concentrations and enhanced penetration of 1,4-dioxane into the low-k zones relative to 1,1,1-TCA within the downgradient plume. Data from focused characterization studies at two different field sites confirmed that a significant amount of the 1,4-dioxane mass was associated with lower-k zones within and adjacent to the more transmissive portions of the aquifers.

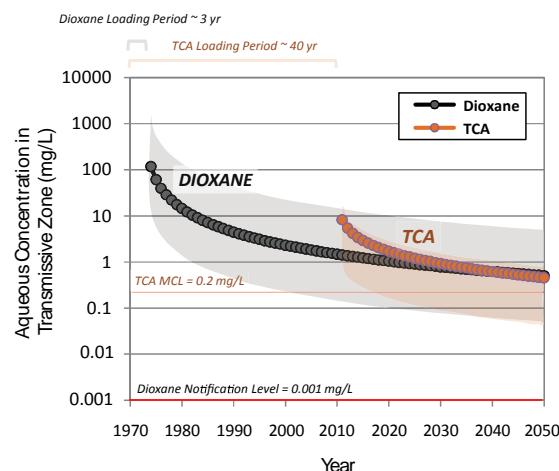


Figure 3. Concentrations in source zone aquifer resulting from back diffusion of 1,4-dioxane and 1,1,1-TCA from low-permeability soils during modeled release scenario. 1,4-dioxane predicted to remain orders-of magnitude above potential regulatory levels even 80 years after release (modified from Adamson et al., 2016).

IMPLICATIONS FOR SITE MANAGEMENT: The results indicate that 1,4-dioxane within transmissive portions of the source zone can be depleted quickly due to characteristics that favor both diffusion-based storage and groundwater transport. The modeling results also highlight the potential differences between 1,4-dioxane and chlorinated solvent source zones. For 1,4-dioxane, there may be much less mass in a defined source zone, and the remaining mass will be harder to treat using conventional means. Instead, many sites may be dominated by long-term back diffusion of 1,4-dioxane mass from these “secondary sources”. At a minimum, characterization efforts and conceptual site models for 1,4-

dioxane must include this mass in lower-k zones. These findings also suggest strategies such as natural attenuation may be more practical.

FINDING #5: There is extensive evidence for 1,4-dioxane attenuation at field sites. The conventional conceptual model for 1,4-dioxane is that it is persistent and that limited attenuation would be expected to occur in groundwater. Temporal concentration changes were used to estimate attenuation rates at California GeoTracker sites and monitoring wells at Air Force installations. Statistically-significant positive source attenuation rates for 1,4-dioxane were confirmed at 22 sites (median equivalent half-life = 20 months) (**Figure 4**). At sites where chlorinated solvents and 1,4-dioxane were both present, the median value of all statistically-significant dioxane source attenuation rates was similar to 1,1-DCE and TCE (but lower than 1,1,1-TCA). Attenuation rates based on well-specific records from the Air Force dataset (**Figure 4**) confirmed significant 1,4-dioxane attenuation (131 out of 441 wells) at a similar frequency and extent (median equivalent half-life = 48 months) as observed at the California sites.

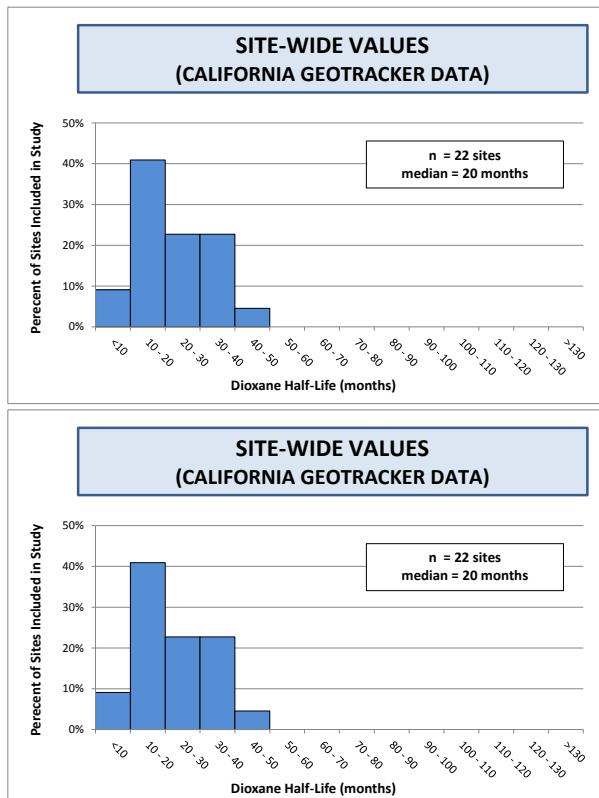


Figure 4. Distribution of 1,4-dioxane half-lives at sites (left) and wells (right) where statistically-significant positive attenuation rates were established (modified from Adamson et al., 2015).

IMPLICATIONS FOR SITE MANAGEMENT: While 1,4-dioxane attenuation was not observed at all sites (in part due to fairly short monitoring records for 1,4-dioxane), the evidence was sufficient enough to question the common belief that 1,4-dioxane is recalcitrant. These findings support the potential viability of natural attenuation as a long-term site management strategy. At a minimum, remedial decision-making should consider the use of recently-developed biomarkers to assess aerobic 1,4-dioxane degradation because it may be an important contributor to site-specific natural attenuation capacity.

FINDING #6: Several factors influencing 1,4-dioxane attenuation at field sites have been confirmed. Based on the analysis of California sites, there was little indication that chlorinated solvent remedial efforts (e.g., chemical oxidation, enhanced bioremediation) impacted 1,4-dioxane attenuation. However, a statistical analysis of different factors that could potentially impact 1,4-dioxane attenuation found a positive correlation between increasing concentrations of dissolved oxygen and 1,4-dioxane attenuation at the Air Force wells. This same analysis found that 1,4-dioxane attenuation negatively correlated with higher metals and CVOC concentrations.

IMPLICATIONS FOR SITE MANAGEMENT: The results from this field-based survey corroborate the results of the lab-based research showing that 1,4-dioxane degradation is favored under aerobic conditions but is inhibited by the presence of chlorinated solvents and metals. Removal of these inhibitory compounds may be key to promoting 1,4-dioxane attenuation at field sites and should be considered as part of the site management strategy.

FINDING #7: If 1,4-dioxane treatment is necessary, then treatment trains may provide a more effective approach. 1,4-dioxane's structure makes it resistant to reductive-based degradation mechanisms, but it is subject to oxidative attack. In situ oxidation technologies (e.g., chemical oxidation, enhanced aerobic biodegradation) should degrade 1,4-dioxane but each has inherent limitations. This study looked at overcoming these limitations by using combinations of technologies, or "treatment trains" that were tested in a series of bench-scale treatability assays. Based on these results, the most promising treatment train was in situ oxidation followed by bioaugmentation with a 1,4-dioxane degrading culture (**Figure 5**). Pre-treatment using chemical oxidation degraded a portion of the 1,4-dioxane, but importantly, degraded the chlorinated solvents. By removing these inhibitors of 1,4-dioxane biodegradation, the bioaugmentation culture thrived and continued to degrade 1,4-dioxane indefinitely. In the absence of chemical oxidation, the undegraded chlorinated solvents completely inhibited 1,4-dioxane biodegradation.

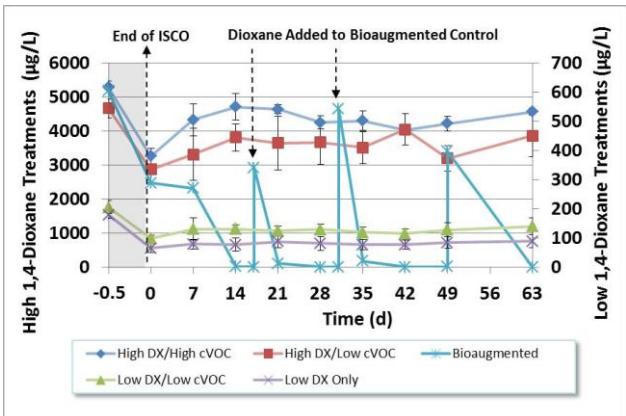


Figure 5. Example of 1,4-dioxane degradation during chemical oxidation (with H_2O_2) and biodegradation “treatment train”. No native 1,4-dioxane degradation capacity was observed. Bioaugmentation with CB1190 resulted in repeated 1,4-dioxane degradation because pre-treatment with oxidant removed all inhibitory chlorinated solvents. Bioaugmentation without chemical oxidation resulted in no 1,4-dioxane degradation due to presence of chlorinated solvents (data not shown).

Project-Generated Articles and Related Content

Adamson, D. T., Mahendra, S., Walker, K., Rauch, S., Sengupta, S., and Newell, C. (2014). A Multi-Site Survey to Identify the Scale of the 1, 4-Dioxane Problem at Contaminated Groundwater Sites. *Environmental Science & Technology Letters*, 5: 254-258.

Adamson, D. T., Anderson, R. H., Mahendra, S., and Newell, C. J. (2015). Evidence of 1, 4-dioxane attenuation at groundwater sites contaminated with chlorinated solvents and 1, 4-dioxane. *Environmental Science & Technology*, 49(11), 6510-6518.

Adamson, D. T., de Blanc, P. C., Farhat, S. K., and Newell, C. J. (2016). Implications of matrix diffusion on 1, 4-dioxane persistence at contaminated groundwater sites. *Science of The Total Environment*, 562, 98-107.

Anderson, R. H., Anderson, J. K., & Bower, P. A. (2012). Co-occurrence of 1, 4-dioxane with trichloroethylene in chlorinated solvent groundwater plumes at US Air Force installations: Fact or fiction. *Integrated environmental assessment and management*, 8(4), 731-737.

IMPLICATIONS FOR SITE MANAGEMENT:

Conventional treatment methods may be challenging to implement at many 1,4-dioxane sites where concentrations are dilute and/or dominated by matrix diffusion. However, for sites where high-concentration source zones have been identified, or where regulatory and risk drivers exist, treatment trains should be considered as a viable approach for co-occurring 1,4-dioxane and chlorinated solvents. Targeted chemical oxidation may prove beneficial for subsequent biologically-based approaches, including both enhanced bioremediation and natural attenuation.

FOR MORE INFORMATION

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[https://serdp-estcp.org/index.php/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2307/ER-2307/\(language\)/eng-US](https://serdp-estcp.org/index.php/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2307/ER-2307/(language)/eng-US)

Project Report (including all results):

Anticipated December 2016



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